

THE DETERMINATION OF VOLATILE ACIDS

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Ontario

Ministry
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Laboratory
Branch

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THE DETERMINATION OF VOLATILE ACIDS

The anaerobic degradation of carbohydrates, proteins and fats by saprophytic bacteria produces by-products such as volatile fatty acids, ammonia, alcohols, hydrogen sulfide, methane and carbon dioxide. Volatile fatty acids are short chain structures of low molecular weight and include acetic, propionic, butyric and to a lesser extent valeric, isovaleric and caproic acids. These fatty acids are termed "volatile acids" because they can be distilled at atmospheric pressure.

Volatile acid data is useful in interpreting the performance of anaerobic waste treatment processes at sewage treatment plants. Ideally, a certain level of volatile acids must be maintained in order to keep the anaerobic digestors operating efficiently.

1. Sample Handling and Preservation

Samples for volatile acids determination should be submitted in wide-mouthed jars and kept refrigerated prior to analysis.

2. Selection of Method

The laboratory currently uses the column partition chromatography method for the determination of volatile acids. Gas chromatographic techniques are available which are capable of detecting individual acid components at extremely low concentrations; however, these techniques are unsuitable for routine analysis.

THE DETERMINATION OF VOLATILE ACIDS
COLUMN PARTITION CHROMATOGRAPHY METHOD

SUMMARY

Substance determined.	Volatile acids expressed as <i>mg/l</i> acetic acid.
Interpretation of results.	Volatile acids are short chained organic acids; the test procedure does not differentiate among the chemical species, and the results are expressed as <i>mg/l</i> acetic acid. In an efficient anaerobic digestion system, the concentration level of volatile acids is relatively constant for any given treatment plant; a sharp increase or upward drift in the volatile acid concentration warns the operator of impending trouble.
Principle of method.	An acidified aqueous sample containing organic acids is adsorbed on a column of granular inert silicic acid. A chloroform-n-butanol solvent is passed through the column to elute the organic acids. The eluate is collected and titrated with standard <i>0.02N</i> sodium hydroxide to the phenolphthalein endpoint.
Time required for analysis.	A single analysis requires <i>30 minutes</i> . A batch of <i>seven</i> samples can be analyzed in <i>two hours</i> .
Range of application.	A <i>5.0 ml</i> aliquot of filtered or centrifuged sample is required for the test. This will cover a range of <i><50</i> to <i>several thousand mg/l</i> of volatile acids.
Standard deviation.	<i>490 ± 5 mg/l</i> for <i>ten</i> determinations performed on a standard containing <i>500 mg/l</i> acetic acid.
Accuracy.	Not less than <i>95%</i> on an acetic acid standard.
Limit of detection.	<i>50 mg/l</i> volatile acids as acetic acid.

Interferences
and shortcomings.

The chloroform-n-butanol solvent system is capable of eluting organic acids other than volatile acids and some other synthetic detergents. Fortunately, the concentrations of these non-volatile components are insignificantly low.

Minimum volume
of sample.

Sufficient sample to provide 10 ml of supernatant.

Preservation and
sample containers.

Samples should be submitted in wide-mouth jars and kept refrigerated prior to analysis.

THE DETERMINATION OF VOLATILE ACIDS

1. Introduction

An aqueous sample, obtained by centrifuging or vacuum-filter, is acidified and adsorbed on a previously prepared silicic acid column. The volatile acids are then eluted with a chloroform-n-butanol solvent. The eluate is collected and titrated with standardized 0.02N NaOH to the phenolphthalein endpoint.

2. Interferences and Shortcomings

Positive interferences may arise since the chloroform-n-butanol solvent is capable of eluting other organic acids (crotonic, adipic, pyruvic, phthalic, fumaric, lactic, succinic, malonic, gallic, aconitic and oxalic) as well as some synthetic detergents. However, these components are present only in small quantities.

Atmospheric carbon dioxide may affect the titration extensively if a sample is subjected to excessive agitation. Extreme care must be exercised to avoid vigorous mixing of the sample during titration.

3. Apparatus

- a) Centrifuge or filtering assembly.
- b) Gooch or fritted glass crucibles.
- c) Separatory funnel, 1000 ml.
- d) Volumetric pipets, 5.0, 10.0 ml.
- e) Erlenmeyer flask, 250 ml.
- f) Gooch or fritted glass crucible adapters.

4. Reagents

- a) Silicic acid, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, 50 - 200 mesh.
- b) Chloroform, CHCl_3 , reagent grade.
- c) n-Butanol, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, reagent grade.
- d) Sulfuric acid, H_2SO_4 , concentrated, reagent grade.
- e) Thymol blue indicator.
- f) Phenolphthalein indicator.
- g) Methanol, CH_3OH , reagent grade.
- h) Sodium hydroxide, NaOH , reagent grade.
- i) Chloroform-n-Butanol Reagent:
Mix 300 ml reagent grade chloroform, 100 ml n-butanol and 80 ml 0.5 N H_2SO_4 in a separatory funnel. Drain off the lower organic layer through a fluted filter paper into a dry amber reagent bottle.
- j) Thymol Blue Indicator Solution:
Dissolve 80 mg thymol blue in 100 ml absolute methanol.
- k) Phenolphthalein Indicator Solution:
Dissolve 80 mg phenolphthalein in 100 ml absolute methanol.
- l) Stock Standard Sodium Hydroxide: (1.0N)
Dissolve 40 g NaOH in deionized distilled water and dilute to 1000 ml.
- m) Standard Sodium Hydroxide: (.02N)
Dilute 20 ml of 1.0N NaOH stock solution to 1 liter with absolute methanol. Standardize this working solution against potassium biphthalate.

5. Procedure

- a) Centrifuge or vacuum-filter enough sludge to obtain 10 - 15 ml clean filtrate in a small beaker.
- b) Add two to four drops of thymol blue indicator solution, then concentrated H_2SO_4 dropwise, until color changes from red to thymol blue (pH 1.0 - 1.2).

c) Column chromatography:

- i) Place approximately 12 g silicic acid in a fritted glass crucible.
- ii) Apply suction to pack the column.
- iii) With a 5.0 ml volumetric pipet, distribute the acidified sample evenly over the surface of the column.
- iv) Decrease the vacuum as soon as the last portion of the sample has entered the column.
- v) Quickly add 65 ml chloroform-n-butanol reagent over the surface of the column, making sure that the silicic acid is kept under the solvent throughout the process.
- iv) Discontinue the suction just before the last portion of the chloroform-n-butanol reagent enters the column.

d) Titration

- i) Remove the filter flask from the unit.
- ii) Titrate the contents with standard 0.02N NaOH to a phenolphthalein endpoint which should last for at least 30 seconds. Avoid aeration of the sample.

e) Blank

Prepare a blank consisting of 5.0 ml acidified (H_2SO_4) distilled water and repeat procedure from step c), part (v).

6. Calculation and Reporting

$$\text{Total volatile acids (mg/l as acetic acid)} = \frac{(a - b)N \times 60 \times 1000}{5}$$

where a = ml NaOH used for sample

b = ml NaOH used for blank

N = Normality of NaOH

Results are reported to the nearest 5 mg/l.

7. Precision

Average recoveries of about 95% are obtained for organic acid concentrations above 200 mg/l expressed as acetic acid. Titration precision expressed as the standard deviation is about ± 0.1 ml or approximately 25 mg/l expressed as acetic acid.

8. Bibliography

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- ii) *Water Research*, Pergamon Press 1968, Volume 2, pp. 631-636.
- iii) *Chemistry for Sanitary Engineers*, 2nd ed. McGraw-Hill pp. 479-485.



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